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LASER SPECTROSCOPY OF TRANSIENT MOLECULES IMPORTANT IN
EXPLOSIONS(U) ARIZONA UNIV TUCSON DEPT OF CHEMISTRY
P F BERNATH 28 MAR 86 N00014-84-K-0012

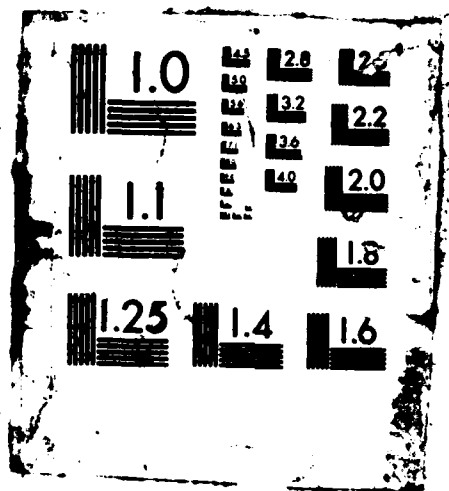
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REPORT DOCUMENTATION PAGE

1a. AD-A178 493		1b. RESTRICTIVE MARKINGS	
2a. AD-A178 493		3. DISTRIBUTION/AVAILABILITY OF REPORT UNLIMITED - UNCLASSIFIED - APPROVED FOR PUBLIC RELEASE	
2b. AD-A178 493		4. PERFORMING ORGANIZATION REPORT NUMBER(S)	
5. MONITORING ORGANIZATION REPORT NUMBER(S)		6a. NAME OF PERFORMING ORGANIZATION University of Arizona	
6b. OFFICE SYMBOL (if applicable)		7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry Tucson, AZ 85721		7b. ADDRESS (City, State, and ZIP Code)	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (if applicable)	
9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N 00014-84-K-0012		10. SOURCE OF FUNDING NUMBERS	
8c. ADDRESS (City, State, and ZIP Code) Arlington, VA 22217		PROGRAM ELEMENT NO 61153N	PROJECT NO. RR 011-03-OD
		TASK NO	WORK UNIT ACCESSION NO NR 602-015
11. TITLE (Include Security Classification) Laser Spectroscopy of Transient Molecules Important in Explosions (Unclassified)			
12. PERSONAL AUTHOR(S) Peter F. Bernath			
13a. TYPE OF REPORT Annual - #3	13b. TIME COVERED FROM 1/1/86 TO 12/31/86	14. DATE OF REPORT (Year, Month, Day) March 20, 1986	15. PAGE COUNT Four
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		explosives, Free radicals	
		detonations, Fourier transform spectroscopy	
		Laser-induced fluorescence	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Work on the spectra of the radicals NH, CCN, PH and CP is complete and in press. The vibration-rotation spectrum of CH was analyzed. The ultra-cold emission spectrum from the jet-cooled CH ₃ N and CD ₃ N radical was recorded and analyzed. The first gas-phase metal azides CaNNN and SrNNN were discovered. (keywords:)			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a. NAME OF RESPONSIBLE INDIVIDUAL Peter F. Bernath		22b. TELEPHONE (Include Area Code) (602) 621-2115	22c. OFFICE SYMBOL

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A. The Free Radicals: NH, CCN, CP and PH.

The spectra of these free radicals were described in previous reports. The work on these species is complete and published or in press.¹⁻⁵

B. The Vibration-Rotation Spectrum of CH.



The CH radical is one of the most prominent and important molecules in detonations and all varieties of energetic environments. In spite of the frequent observation of the spectra of CH in many regions of the electromagnetic spectrum (microwave to ultraviolet), the excited vibrational levels of the ground state are essentially uncharacterized with the exception of $v=1$. Since these excited vibrational levels will be populated in energetic environments, it is important to detect them spectroscopically. The vibration-rotation emission spectrum of the $X^2\Pi$ state of CH was observed with the McMath Fourier transform spectrometer at Kitt Peak. The 1-0, 2-1 and 3-2 bands were detected in a microwave discharge of allene in Ar and methane in He. A simultaneous fit of all of the line positions provided spectroscopic constants for $v=0, 1, 2$ and 3. Equilibrium molecular constants (in cm^{-1}) include $\omega_e = 2860.4118(98)$, $\omega_e x_e = 64.1082(46)$, $\omega_e y_e = 0.2406(10)$, $B_e = 14.45862(48)$, $\alpha_e = 0.53416(58)$, $\gamma_e = 0.00198(15)$, $r_e = 1.11983(2)\text{\AA}$. An RKR potential curve was calculated from the equilibrium constants.

C. Methylnitrene: CH₃ and CD₃N

Metal and organic azides are widely used energetic materials. The primary decomposition products of organic azides are nitrene free radicals R-N.

The CH₃N and CD₃N radicals were made in a free radical jet source of the Engelking type. A corona-excited plasma produced from methyl azide (CH₃N₃ or CD₃N₃) in He was expanded into vacuum to provide ultracold (15K) CH₃N and CD₃N. The low rotational temperature simplifies the spectrum and allows a rotational analysis.

The CH₃N radical is closely related to NH so there is an ultraviolet $\tilde{X}^3E-\tilde{X}^3A_2$ transition analogous to the $A^3\Pi-X^3\Sigma^-$ transition of NH. The ultraviolet emission from the cold plasma was detected with the Fourier Transform spectrometer. The laser excitation spectrum was also recorded with a frequency-doubled c.w. ring dye laser. Preliminary analysis of $\tilde{X}-\tilde{X}$ spectrum of CH₃N and CD₃N gives an r_0 structure of $r_{C-N} = 1.411\text{\AA}$, $r_{C-H} = 1.09\text{\AA}$ (assumed) and $\theta_{CH_2} = 106^\circ$ for the ground state. The C-N bond length is somewhat shorter (0.03-0.09 \AA) than the values predicted by three recent quantum chemical calculations.

D. New Organometallic Free Radicals: CaNNN and SrNNN

We have continued work on the alkaline earth-containing free radicals such as MOR, MNCO and MC₅H₅ (M = Ca, Sr; R = CH₃, CH₂CH₃, etc.) that we have discovered with partial ONR support. The first spectrum of a gas-phase metal azide was recorded by the reaction of Ca (or Sr) with HN₃ to produce

CaNNN (or SrNNN). Metal azides are widely used in detonators.

A high-resolution analysis of the $\tilde{\chi}^2_{\Pi}-\tilde{\chi}^2_{\Sigma}+$ transition of SrNNN established a linear geometry with a Ca-N bond length of 2.25 Å. The Sr-N vibrational frequency is 316 cm⁻¹.

References

1. R. S. Ram, C. R. Brazier and P. F. Bernath, Fourier Transform Spectroscopy of the $A^3\Pi-X^3\Sigma^-$ Transition of NH, J. Mol. Spectrosc. 120, 381-402 (1986).
2. R. S. Ram and P. F. Bernath, Fourier Transform Spectroscopy of NH: The $c^1\Pi-a^1\Delta$ Transition, J. Opt. Soc. B., 3, 1170-1174 (1986).
3. C. R. Brazier, L. C. O'Brien and P. F. Bernath, Fourier Transform Detection of Laser-Induced Fluorescence from the CCN Free Radical, J. Chem. Phys., in press.
4. R. S. Ram and P. F. Bernath, Fourier Transform Spectroscopy of the $A^2\Pi-X^2\Sigma^+$ System in CP, in press, J. Mol. Spectrosc.
5. R. S. Ram and P. F. Bernath, Infrared Fourier Transform Spectroscopy of PH, in press, J. Mol. Spectrosc.
6. P. F. Bernath, The Vibration-Rotation Emission Spectrum of $CH(X^2\Pi)$, in press, J. Chem. Phys.
7. P. G. Carrick, C. R. Brazier, P. F. Bernath and P. C. Engelking, The Structure of the Methylnitrene Radical, submitted, J. Am. Chem. Soc.
8. C. R. Brazier, P. F. Bernath, S. Kinsey-Nielsen and L.C. Ellingboe, Laser Spectroscopy of Alkaline Earth Monoalkoxide Free Radicals, J. Am. Chem. Soc. 108, 2126-2132 (1986).
9. L. C. Ellingboe, A.M.R.P. Bopegedera, C. R. Brazier and P. F. Bernath, Laser Spectroscopy of Alkaline Earth Monocyanates, Chem. Phys. Lett. 126, 285-289 (1986).
10. L. C. O'Brien and P. F. Bernath, Laser Spectroscopy of Calcium and Strontium Monocyclopentadienides, J. Am. Chem. Soc. 108, 5017-5018 (1986).
11. C. R. Brazier and P. F. Bernath, Laser Spectroscopy of Calcium and Strontium Monoazides, in preparation.

STATUS REPORT

for period

Jan 1, 1986 - Dec 31, 1986

for Contract N00014-84-K-0122

LASER SPECTROSCOPY OF TRANSIENT MOLECULES IMPORTANT IN EXPLOSIONS

A. Graduate Students

1. L. Ellinboe (O'Brien)
2. D. Bopegedera
3. S. Pianalto

B. Post-Doctorals

1. C. Brazier
2. R. Ram
3. P. Carrick (visitor)

C. Current Grant Support

National Science Foundation, 1986 - 1989, \$280,000

Petroleum Research Fund, 1985 - 1988, \$52,500

D. Financial Status

All funds were expended by December 31, 1986.

E. Permanent Equipment

None acquired.

STATUS REPORT

A. Personnel

Peter Bernath, P. I., Assistant Professor, summer support

Chris Brazier, postdoctoral research associate, half-time support

Ram Ram, postdoctoral research associate, half-time support

Susan Kinsey-Nielsen, graduate student (M. Sc. degree this year)

Leah Ellingboe, graduate student

Darshi Bopegedera, graduate student

B. Current Grant Support

National Science Foundation, 1983-1986, \$180,000

Petroleum Research Fund, 1985-1988, \$52,500

C. Financial Status

All funds will be expended by December 31, 1985.

D. Permanent Equipment

Ultraviolet capability (doubling crystals) for Coherent 699-29 dye laser,
\$10,010.

END

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